distributions of the borohydride reduction of ketones with only one transition state.

The approach used here is not limited to the treatment of the ketone reduction. It is possible to adapt the parameters to other nucleophiles and other functional groups, such as double bonds. It should therefore be of general interest in mechanistic and synthetic chemistry.

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H/D Exchange in Electrolytic Reduction Reactions of Phenyl Ketones[1]

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Abstract: Reduction of phenacyl chloride in DMF containing 1% D_2O is electrochemically irreversible. The observed products at the reduction potential are acetophenone plus dimeric product. Recovery of the ketone after short reaction times reveals the presence of considerable H/D exchange of the methylene hydrogens in competition with the reduction reaction. Similarly, in the reduction of 1,2-diphenylpropanone, which proceeds with asymmetric induction, H/D exchange of the α hydrogen is very important. The exchange process appears to be part of the electrochemical reaction and is associated with the first electron transfer step.

A survey of the electrochemical literature reveals that studies on "electrochemical irreversible" systems do not provide evidence for the presence of reactions which regenerate the starting material from the reaction intermediate. This situation is not expected with those electrochemically irreversible cases where one and only one reaction pathway is available for the oxidation-reduction process as is usually the case with metal cations. However, in the case with larger organic molecules more than one reaction pathway may be available for the oxidation-reduction process. Even with these cases no evidence of the regeneration reaction is available. For example, the electrolytic reductions of alkyl halides is presumed to proceed with no regeneration of RX from $RX^{-}\cdot$. And while the more facile reduction of halides which are allylic, benzylic, or α to a carbonyl is associated with the formation of an initially formed radical ion, no evidence of regeneration is available (eq 1).[2,3] We now present the results of a study aimed at establishing the relative importance of reactions which regenerate the alkyl halide from the radical ion. For technical convenience the easily reducible phenacyl chloride was studied using a platinum electrode in order to avoid the usual adsorption and mercuration problems of the mercury electrode[3] and in moist dimethylformamide in order to avoid solvent problems.[4]

$$RX \overset{+e}{\rightleftharpoons} [RX^{-}\cdot] \rightarrow R\cdot + X^{-} \rightarrow \rightarrow RH \qquad (1)$$

Results and Discussion

Phenacyl Derivatives. All electrochemical reductions were performed using a PAR Model 170. The electrolysis experiments were performed in DMF containing the appropriate amount of D_2O or CH_3OD plus 0.1 M tetraethylammonium fluoroborate. As seen in Figure 1, cyclic voltammetry of phenacyl chloride (10^{-3} M) using a platinum button as the working electrode shows electrochemical irreversibility at scan rates between 0.1 and 10 V/s. E_{pc} appears at -2.0 V with $I_p/V^{1/2}C$ equal to 0.19 A $s^{1/2}/V^{1/2}M$ at a scan rate of 200 mV/s. With these DMF-D_2O solutions used, the background currents become significant at -2.5 V and finally break down at -2.8

Table I. Controlled-Potential Electrolysis of Phenacyl Chloride in DMF[a] at 23 °C

			Fraction reaction		
Conditions[b]	Faraday/mol	Conversion	Exchange, f_{ex}[c]	Reduction, f_r	Condensation, f_c
−0.6 V 250 s	<0.001	0.56	<0.03		0.56
−1.8 V 250 s	0.12	0.95	0.05		0.9
−2.0 V 420 s	0.15	0.4	0.34	0.02[d]	0.04
−2.2 V 120 s	0.05	0.12	0.12	0.005	
−2.2 V 120 s (4% D_2O)	0.05	0.18[d]	0.18	0.005	

[a] 0.01 M RCl plus 0.1 M Et_4NBF_4 plus 1% D_2O. [b] Potential at platinum electrode vs. Ag/Ag^+ (0.01 M). [c] Fraction exchange of two hydrogens in the recovered RCl. [d] Mixture contains a trace of dimeric product.

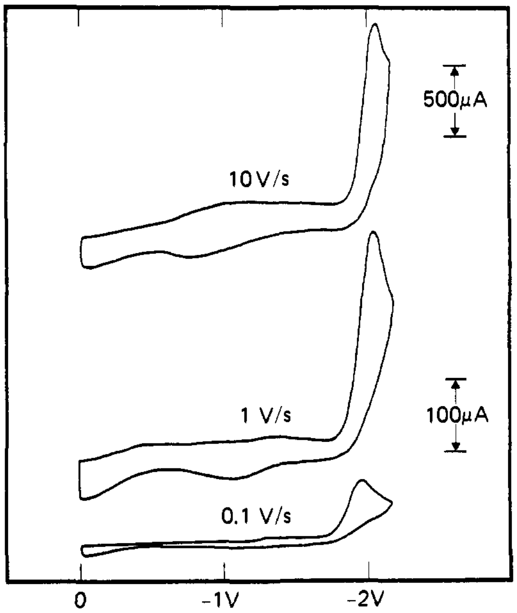
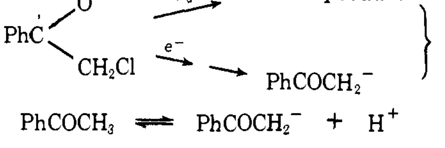


Figure 1. Cyclic voltammograms of $PhCOCH_2Cl$ in 1% D_2O-DMF using Pt vs. Ag/Ag^+ (0.1 M) electrodes with *iR* compensation.

V. Controlled potential electrolysis experiments were performed in a two-compartment cell using a platinum gauze. After the electrolysis period the ketone mixture was recovered and the extent of reaction was determined by GLC analysis. In a typical reaction, phenacyl chloride is recovered along with some produced acetophenone and some high molecular weight material. No carbinols are found where phenylethyl and α-chlorophenylethyl alcohols are easily detected to ca. 0.1%. That the acetophenone is not further reduced in this reaction is reasonable since under these conditions the E_{pc} for acetophenone is −2.6 V. The reaction appears quantitative by GLC analysis and the ketone mixture was isolated in 85% yield.



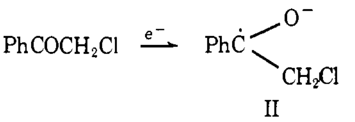
$$\mathrm{Ph\dot{C}}\begin{smallmatrix}\mathrm{O^-}\\ \mathrm{CH_2Cl}\end{smallmatrix} \left.\begin{matrix}\xrightarrow{f_d} \text{dimeric product}\\ \xrightarrow{e^-} \xrightarrow{} \mathrm{PhCOCH_2^-}\end{matrix}\right\} \qquad (2)$$

$$\mathrm{PhCOCH_3} \rightleftharpoons \mathrm{PhCOCH_2^-} + \mathrm{H^+} \qquad (3)$$

NMR analysis of the recovered material shows signals for the aromatic hydrogens which do not appear much different from those for a pure phenacyl chloride sample. The reduction of the α-methylene signal was used to estimate the amount of deuterium incorporation during the electrolysis. No other major signals were visible.

As can be seen in Table I the fraction of phenacyl chloride converted to acetophenone, f_r, is always much less than the fraction of deuterium incorporated into the methylene group of phenacyl chloride, f_{ex}. Of particular interest is the fact that the exchange is in *excess* of Faraday consumption. Thus electrolysis of RCl at −2.2 V in DMF containing 1% (0.5 M) D_2O for 120 s consumes 0.046 Faraday/mol RCl and produces 0.5% acetophenone plus 12% exchange. Thus, exchange in excess of current flow suggests that it either proceeds via a thermal acid-base route distinct from the electrochemical process (eq 4) or via a radical anion (II) which can produce several H/D exchange events per electron transfer.

$$\mathrm{PhCOCH_2Cl} \rightleftharpoons \underset{\mathrm{I}}{\mathrm{PhCOCHCl^-}} + \mathrm{H^+} \qquad (4)$$



$$\mathrm{PhCOCH_2Cl} \xrightarrow{e^-} \underset{\mathrm{II}}{\mathrm{Ph\dot{C}}\begin{smallmatrix}\mathrm{O^-}\\ \mathrm{CH_2Cl}\end{smallmatrix}} \qquad (5)$$

At potentials below E_{pc}, the high proportions of condensation product (f_c) accompanying H/D exchange during the electrolysis suggest a thermal base-catalyzed reaction. The observed exchange plus condensation reactions occur considerably faster than is estimated by the enolization rate constant of ca. $2 \times 10^{-4}\ s^{-1}$.[5] The results are not influenced by changes in the base used. Thus the same results are observed using D_2O or CH_3OD in DMF, NaOMe plus D_2O in DMF, and finally anhydrous CD_3CN in the absence of added base. The observations suggest that the reactions occur primarily at the electrode surface with little influence by the bulk solution environment and that the electrode surface must have a very basic environment.

In contrast, electrolysis at −2.2 V produces exchange and acetophenone product and only small amounts of condensation product. Here again the reaction is not influenced by the base content of the bulk solution. At these potentials, an electrochemical route to H/D exchange must be present.

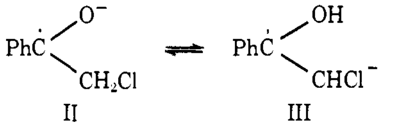
A mechanism consistent with these results involves tautomerism of radical anion II to produce III which can in turn undergo a series of protonation/deprotonation reactions (eq 6 and 7). Since the potential required for reduction of the enol is much more negative than the voltage being applied here, the deuterated radical anion III is reoxidized to regenerate deuterated phenacyl chloride by transferring an electron to another molecule or to the electrode. An alternative explanation is that the initially formed radical anion (II) detaches a hydrogen atom and leaks into the thermal enolization process by generating enolate I (eq 10) in competition with ionization of the chloride ion to generate the phenacyl radical which produces acetophenone and dimer. This process will give rise to exchange

Table II. Electroreduction of Various Phenacyl Derivatives in DMF Containing 0.1 M Et_4NBF_4[a]

			Control potential electrolysis[d]		
	$E_{pc/2}$, V[b]	$i/V^{1/2}C$[b,c]	Conditions	Products	Faraday/mol
$PhCOCH_2Br$	−1.07	64	−1.30 V	18% exchange (2 H)	
	−1.94	150	2 min	No reduction	
$PhCOCH_2Cl$	−1.20	107	−2.20 V	12% exchange (2 H)	
	−1.99	170	2 min	0.5% reduction	0.05
				Trace dimer	
$PhCOCH_2OAc$	−1.94	123	−2.30 V	23% exchange (2 H)	0.03
	−2.30	71	2.5 min	0.2% reduction	
$PhCOCH_3$	−1.98	178	−2.60 V	56% exchange (3 H)	*e*
	−2.42	340[d]	12 min	7% dimer	

[a] Pt vs. Ag/Ag^+ (0.01 M). [b] 0.5 V/s scan rate. [c] $mA/(V/s)^{1/2}M$. [d] DMF containing 1% D_2O. [e] At this potential the solvent is decomposing.

and to the extent that "H·" can reduce a second molecule of phenacyl chloride, exchange will occur in excess of current consumption.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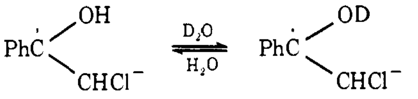
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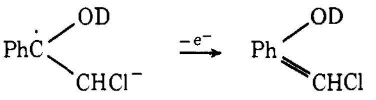
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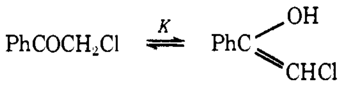
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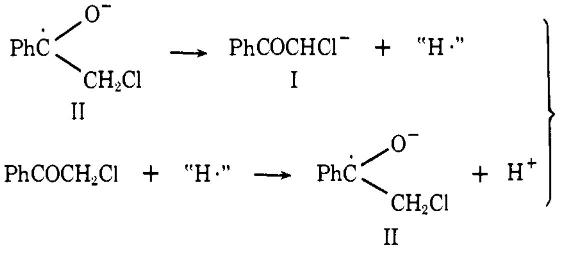

(10)

The driving force for the hydrogen atom detachment reaction can be estimated from the relative stabilities of I and II. As for I, from the available pK_a values for acetophenone (19)[5] and water (16)[6] in aprotic solvents, the $[PhCOCHCl^-]/[PhCOCH_3]$ is estimated as equal to 10^{-11} when the solution contains 1 M H_2O. This indicates that I is 15 kcal less stable than phenacyl chloride. As for II, assuming that the reduction potential for phenacyl chloride (−2.0 V) approximates the thermodynamic potential, then II is ca. 46 kcal less stable then phenacyl chloride. Comparison of these results suggests that formation of I from II can be exothermic by 30 kcal.

The f values from Table I were converted to relative k's assuming pseudo-first-order dependence for the competitive reactions of phenacyl chloride radical anion (II) for entry into the product-forming sequence ($f_r + f_c$) and into the exchange process (f_{ex}). The resulting relative k ratios of ca. 30 suggest that regeneration of starting RCl from II is ca. 2 kcal more facile than dechlorination.

$$k_{ex}/k_{prod} = 2 \log [1 - f_{ex}]/\log [1 - (f_r + f_d)] \quad (11)$$

In an attempt to capture the reaction intermediate, phenacyl chloride was electrolyzed in anhydrous DMF containing 1-5% v/v acetic anhydride. The product mixture recovered after electrolyzing for 30 min at −2.2 V contained 21% acetophenone, 56% acetophenone enol acetate, plus ca. 13% of another product not characterized. The composition of this mixture is based on GLC analysis and on NMR analysis using the characteristic signals (δ) for the methyl hydrogens in acetophenone (2.56), and the vinyl hydrogens in acetophenone enol acetate (4.04 and 4.50). In a similar manner electrolysis in the presence of dimethyl sulfate produced 60% acetophenone, 18% acetophenone enol ether, plus 22% phenacyl chloride enol ether. Finally, no enol ether products were detected when the reduction was carried out in the presence of methyl iodide. The exact mode of formation of the phenacyl chloride enolate product is not known. However, it is most likely produced by capture of the same intermediate which is captured by D_2O to produce exchanged ketone.[7]

This behavior is general and is observed in the electroreduction of other compounds. In Table II are listed the results for various phenacyl derivatives. In every case exchange occurs in excess of reduction and of current consumption, and there appears to be little variation in the exchange to product ratio for this series of derivatives.

1,2-Diphenylpropanone. The results discussed here appear to be general for electrochemical reductions of carbonyl compounds and will influence the stereochemistry of the α carbon at some stage of the reaction. The question that arises is with regard to the importance of exchange process in those reductions where the chirality of the α carbon is important. With this in mind the reduction of 1,2-diphenylpropanone was studied since the electrochemical reduction of this compound is reported to proceed with asymmetric induction. Thus 1,2-diphenylpropanone was electrochemically reduced in 40% aqueous ethanol containing veranol buffer (pH 8) using a mercury pool electrode.[8] Analysis of the reaction product by infrared spectroscopy revealed that pure *erythro*-1,2-diphenylpropan-1-ol was produced. On the other hand sodium reduction of this ketone in refluxing ethanol produced a carbinol mixture containing 64% erythro and 36% threo isomer.

In repeating this work the electrolysis experiments were performed using 0.1 M KOAc solutions and a Ag/Ag^+ (0.01 M) reference electrode. Cyclic voltammetry using a hanging mercury drop electrode with 10^{-3} M ketone in ethanol solution shows a value for E_{pc} equal to −2.42 V with $i_c/CV^{1/2}$ equal to 0.017 $A/M(V/s)^{1/2}$ using a scan rate of 500 mV/s and with i_a/i_c equal to ca. 0.9. Constant potential electrolysis at −2.5 V using a mercury pool electrode in methanol-*Od* for 3 min consumed 0.07 Faraday/mol. The products were recovered in 90% yield and GLC analysis revealed the presence of 99.3% starting ketone plus 0.7% 1,2-diphenylpropanol. NMR analysis of this material revealed a 26% reduction in the signal for the α hydrogen of the ketone resulting from incorporation of deuterium. Again as in the case with the phenacyl derivatives, electrolysis of this ketone in buffered alcohol produces H/D exchange in excess of current consumption and reduction.

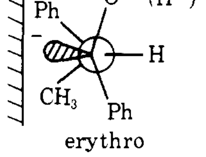
Electrolysis of a similar solution for 2 h consumed 2.5 Faradays/mol. The product mixture was recovered in 80% yield and was conveniently analyzed by NMR without further purification. The relative amounts of ketone, *threo*-ROH, and *erythro*-ROH in the mixture are readily available from the methyl signals (d, $J = 7$ Hz) which appear at δ 1.44, 1.14, and 0.96, respectively. The recovered mixture contained 60% starting ketone, 32% carbinols (62:38 erythro/threo), plus 10% of an unidentified material presumed to be dimeric product. While the same ketone to product composition was available from GLC analysis, the *erythro-/threo-* ROH ratio could not be determined by this method. In 60% aqueous ethanol, electrolysis for 86 min resulted in 80% conversion where the product mixture contained 40% carbinols, with a similar erythro preference, plus 60% of the dimeric material. Solutions with higher water content were not used because of the limited solubility of the ketone.

In repeating the sodium in ethanol reduction using Mandell's procedure, we also find a preference for *erythro*-ROH formation, although smaller than previously reported. The carbinol product was recovered in 70–90% yields and analyzed by NMR as described above. The fraction *erythro*-ROH in the mixture decreased from 57 to 54% as the reaction temperature was reduced from 82 to 45 °C. The remainder of the material was *threo*-ROH. The presence of 0.1 M KOAc does not cause a noticeable change in the produced ratio.

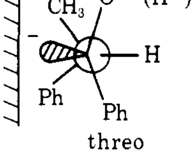
Thus in contrast to previously reported results we find that the electrochemical reduction of 1,2-diphenylpropanone in ethanol shows only a slightly greater preference for *erythro*-ROH formation than the sodium metal reduction reaction. It is of interest to note that preference for *erythro*-ROH is even less than in the reduction reaction with $NaBH_4$ (75% *erythro*-ROH), and with $LiAlH_4$ (90% *erythro*-ROH).[9]

A possible explanation for the discrepancy between our results and those of Mandell may lie in the fact that in highly aqueous solutions electroreduction produces primarily dimeric product which is formed with high geometric specificity.[11] Thus reduction of partly dissolved ketone in 40% aqueous ethanol may produce geometrically pure dimer.

While the electrochemical reduction of ketones proceeds with H/D exchange at the α carbon which involves rehybridization of that carbon and consequently loss of stereochemistry, this process must occur early in the reaction. This conclusion is reached because the results from the product studies suggest that the stereochemistry of the α carbon is intact during the critical step where the reduced carbonyl anion is protonated to produce the carbinol derivative. The exchange process must occur before the second electron transfer step since at this stage of the reaction the stereochemistry of the product is already determined. What is not clear is to what extent the process for protonation of the carbanion is influenced by presence of the electrode surface.[10] However, the similarity between the electrochemical and sodium metal reactions suggest that the surface is not very important in this step.



erythro



threo

Experimental Section

The solvent mixtures used were prepared by mixing the appropriate amount of D_2O with previously dried acetonitrile or DMF.[12] Methanol-*Od* available from Merck Sharp and Dohme was used without further treatment. The electrolytic salts, tetraethylammonium fluoroborate, and potassium acetate were dried before use.

Commercially available phenacyl chloride and bromide were recrystallized from pentane-ethyl ether mixtures: RCl, mp 51–52 °C, lit.[13a] 54 °C; RBr, mp 49–50 °C, lit.[13b] 50 °C. Acetophenone was distilled before use.

Phenacyl acetate was prepared by reacting 3 g of phenacyl chloride in 200 mL of ethanol containing 2 g of sodium acetate for 2 days at 75 °C. The alkyl acetate was recovered by extraction with ethyl ether and recrystallized from pentane-ethyl ether mixture as square plates, mp 48.5–49.5 °C, lit.[14] 48.5–49.5 °C. The NMR spectra had $\delta_{Me_4Si}(CCl_4)$ 7.9–7.5 (m, 5.0, aromatic), 5.12 (s, 2, methylene), and 2.1 (s, 3.1, methyl).

1,2-Diphenylpropanone was prepared as previously described,[15] mp 55–56 °C, lit.[15] 50–51 °C. The NMR spectra had $\delta_{Me_4Si}(CCl_4)$ 8.0–7.8 plus 7.4–7.0 (m, 10, aromatic), 4.49 (q, 1, α-H), and 1.44 (d, 3, methyl); $J_{2,3} = 6$ Hz.

The electrolysis solutions were prepared by mixing the appropriate amount of D_2O or CH_3OD plus tetraethylammonium fluoroborate (0.1 M) with carefully dried DMF. Traces of oxygen were removed from these solutions by sweeping with nitrogen prior to electrolysis. All electrochemical measurements were performed using a PAR Model 170. A two-compartment cell separating the working and counter electrode was used with reference electrode placed in the working electrode compartment. A Micro-Reference silver electrode available from Microelectrodes, Inc., was filled with DMF or CH_3CN solution containing 0.1 M Et_4NBF_4 plus 0.01 M $AgBF_4$. This electrode is +0.3 V compared to the calomel electrode.

The reaction solutions used in constant potential electrolysis were extracted between ethyl ether and water in the usual way and the recovered product mixture was analyzed by NMR and by GLC. The recovered yields ranged 80–90%. GLC analysis for the studies relating to the phenacyl derivatives were performed on a 6 ft × ⅛ in. column packed with 10% UCW98 on CW 80/100 at 110 °C with programming up to 200 °C. For the studies relating to 1,2-diphenylpropanol, the GLC analyses were performed on a 4 ft × ⅛ in. column packed with 10% SE-30 on CQ using temperature programming from 100 to 200 °C.

The NMR spectra for *erythro*-1,2-diphenylpropanol prepared by $LiAlH_4$ reduction of the corresponding ketone had $\delta_{Me_4Si}(CCl_4)$ 7.1–6.9 (m, 10, aromatic), 4.42 (d, 1, α hydrogen), 2.8 (quintet, 1, β hydrogen), and 0.96 (d, 3, methyl) with $J_{1,2} = J_{2,3} \sim 7$ Hz. The NMR signals for *threo*-1,2-diphenylpropanol available by comparison of the spectra of the products from $LiAlH_4$ and electrolytic reductions are $\delta_{Me_4Si}(CCl_4)$ 7.1–6.9 (m, 10, aromatic), 4.52 (d, 1, α hydrogen) 3.36 (quintet, 1, β hydrogen), and 1.16 (d, 3, methyl) with $J_{1,2} = J_{2,3} \sim 7$ Hz.

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